

Communications to the Editor

Carbon Nanotubes as Superior Sorbent for Dioxin Removal

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Received October 31, 2000

Dioxins and related compounds (e.g., polychlorinated dibenzofurans and biphenyls) are highly toxic and stable pollutants. Dibenz-p-dioxins are a family of compounds consisting of two benzene rings joined by two oxygen atoms and having from zero to eight chlorine atoms attached around the rings. The dibenzofurans are a similar family differing in which only one of the bonds between the two benzene rings is bridged by oxygen. The toxicity of dioxins varies with the number of Cl atoms, with non- and monochloro dioxins being nontoxic, while being highly toxic with more Cl atoms. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) is a known human carcinogen, and other dioxins are likely human carcinogens. In addition to cancer, dioxins also adversely affect the immune and endocrine systems and the development of fetuses.¹ Dioxins are mainly generated from the combustion of organic compounds in waste incinerators, such as municipal waste, medical waste, hazardous waste, and army stockpiles (chemical agents). They are formed downstream of the combustion zone with typical concentrations of 10–500 ng/m³. Current regulations on dioxin emissions are complex, depending on the toxic equivalency of the actual compounds and O₂ concentration, and vary in different countries. Nonetheless, removal to well below 1 ng/m³ is generally required.² Since 1991, activated carbon adsorption has been widely adopted for dioxin removal from waste incinerators in Europe and Japan.² Because of the higher bond energy between dioxin and activated carbon than other sorbents, the removal efficiency for dioxin by activated carbon is much higher than other sorbents, such as clays, pillared clays, γ -Al₂O₃ and zeolites.³

Due to the extreme toxicity of dioxins, it is desirable to have a more efficient sorbent than activated carbon so that the dioxin emissions can be reduced to lower levels. In this communication, we have found that the interactions of dioxins with carbon nanotubes are much stronger than that with activated carbon. The results show that carbon nanotubes are a significantly better sorbent than activated carbon for dioxin removal. Carbon nanotubes include single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). They are hollow nanosize tubes and have attracted intense interest since their recent discovery. Large efforts have been devoted to improving their syntheses, determining their structures, measuring their properties, and finding applications.^{4,5} Their unique electronic properties and structure have led to interest in their potential applications. For example, SWNTs were reported to be chemical sensors for NO₂ and NH₃. Upon exposure to gaseous NO₂ or NH₃, the electrical resistance of SWNT was found

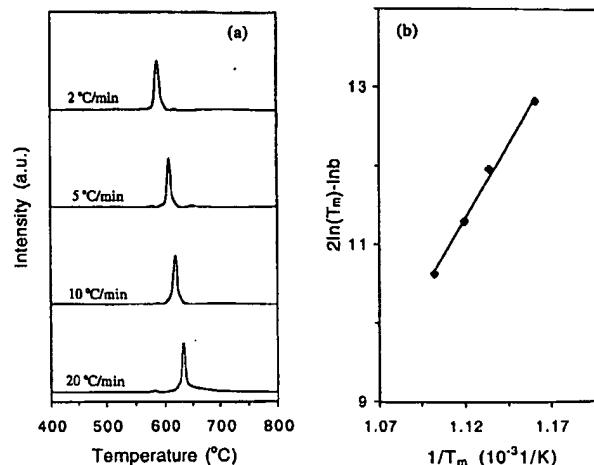
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Figure 1. (a) TPD profiles of dioxin on carbon nanotubes at heating rates of 2, 5, 10, and 20 °C/min. (b) Relationship between the maximum desorption temperature (T_m) and the heating rate (b) for dioxin on carbon nanotubes.

to change (either increasing or decreasing) significantly.⁴ Also, recent reports on hydrogen storage by SWNTs^{5a,c,d} and MWNTs^{5b} are of great interest. In addition, carbon nanotubes have also been studied as quantum nanowires, electron field emitters, catalyst supports, etc.

In this work, we report first data on MWNTs as sorbent for dioxin removal. A technique based on temperature-programmed desorption (TPD) was used for studying dioxin adsorption.³ Because of the high melting- and boiling points of dioxins, it is difficult to generate the vapors and control their concentrations. This makes it difficult to directly measure adsorption isotherms for dioxins using conventional techniques. Moreover, the adsorption bonds for these compounds are generally very strong, and the isotherms are very steep. Information in the very low concentration range, in the parts per trillion (ppt) to ppb range, is extremely difficult to obtain. But for dioxins, information in the ppt range is important because removal to the order of ng/m³ is required. To overcome these difficulties, a simple TPD technique for sorbent screening was developed in our previous work.³ Since the desorption peak temperature is related to the adsorption bond strength, a stronger bond gives rise to a higher TPD peak. From the different desorption peaks at different heating rates, the activation energy for desorption (or the bond energy)

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(6) In each experiment, 0.1 g of carbon nanotubes was loaded in a stainless steel tubing (1/8-in.) with an inner diameter of 2 mm. The non-chloro dioxin was used as the model compound for dioxins. The dioxin solution in *N,N*-dimethylformamide solution was loaded at the inlet of the sorbent column, and the column was purged with helium (50 mL/min) at room temperature. Subsequently, the sample was heated in the He flow at a constant heating rate. As the temperature was increased, the dioxin at the inlet was vaporized and was subsequently adsorbed in the bed. As the temperature was further increased, the dioxin was eventually desorbed. The effluent or the desorption products were analyzed continuously by both a thermal conductivity detector (TCD) and a flame ionization detector (FID) in a gas chromatograph (Shimadzu, 14A).

Table 1. Peak Desorption Temperature of Dioxin at Different Heating Rates, Activation Energies for Desorption and Langmuir Constants on Different Sorbents

sorbent	peak desorption temp. (°C) at different heating rates				desorption activation energy (kJ/mol)	Langmuir constant B at 25 °C (l/atm)	ref
	2 °C/min	5 °C/min	10 °C/min	20 °C/min			
carbon nanotubes	588	609	620	634	315	2.7×10^{52}	this work
ZX-4 carbon (Mitsubishi)	481	517	543	?	119	1.3×10^{18}	3
γ -Al ₂ O ₃	306	353	394	?	47.9	4.5×10^5	3

is calculated, and then the equilibrium adsorption isotherms for dioxins can be estimated. The experiments were carried out from room temperature to 800 °C at different heating rates from 2 to 20 °C/min.⁶ Carbon nanotubes were prepared using catalytic decomposition of methane.⁷ The obtained material was treated with nitric acid to dissolve the catalyst particles and then calcined at 400 °C for 1 h in air. Transmission electron microscopy (TEM) image shows that the prepared carbon nanotubes are MWNTs and the ends of some MWNTs are open. The MWNTs have a BET surface area of 155 m²/g and a pore size distribution from 2.5 to 30 nm (with the first peak at 2.9 nm), obtained from N₂ adsorption isotherms at -196 °C.

Figure 1a shows the TPD spectra of dioxin on carbon nanotubes at different heating rates. The maximum desorption temperature increased from 588 to 634 °C as the heating rate was increased from 2 to 20 °C. According to the following equation⁸

$$2 \ln T_m - \ln b = \frac{E}{RT_m} + \ln ZA \quad (1)$$

(where T_m is the peak desorption temperature, b is heating rate, E is activation energy for desorption, R is the gas constant, and Z is a constant that depends on the desorption kinetics.), the activation energy for dioxin desorption can be calculated. The plot of $[2 \ln T_m - \ln b]$ versus $1/T_m$ is given in Figure 1b. From this plot, the activation energy (E) for desorption of dioxin on the carbon nanotubes is 315 kJ/mol.

For adsorption of low-volatile organic compounds, such as dioxins, the sorbate-surface bond is usually much stronger than the sorbate-sorbate bond. Hence, the adsorption is limited to within a monolayer, and this is particularly the case for low pressures or concentrations. Consequently, the Langmuir isotherm is a meaningful representation for adsorption equilibrium.⁹

$$\theta = \frac{q}{q_m} = \frac{BP}{1 + BP} \quad (2)$$

where θ is fractional surface coverage, q is the amount adsorbed

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at absolute temperature T and vapor pressure P , q_m is the monolayer amount, and B is the Langmuir constant. Once the activation energy for desorption (E) is known, the Langmuir constant B can be calculated by¹⁰

$$B = \frac{\sigma N}{\beta \sqrt{2\pi MRT}} e^{E/RT} \quad (3)$$

where σ is the molecular area, N is Avogadro's number, β is the vibration frequency of the adsorbate against the surface, and M is the molecular weight. From eq 3, the Langmuir constant for dioxin is

$$B = \frac{3.2 \times 10^{-2}}{\sqrt{T}} e^{E/RT} \text{ (l/atm)} \quad (4)$$

The value of B at 25 °C is 2.7×10^{52} l/atm for dioxin on carbon nanotubes. A direct comparison of Langmuir constant B values of dioxin on various sorbents is given in Table 1. It can be seen that desorption temperatures, the desorption activation energy, and the Langmuir constant of dioxin on carbon nanotubes are much higher than those of activated carbon and γ -Al₂O₃. In the Henry's law region, which is the low-concentration regime that is of practical interest, the amount adsorbed on carbon nanotubes is 10³⁴ higher than that on activated carbon. Hence, a significantly higher dioxin removal efficiency is expected with carbon nanotubes than that with activated carbon. The strong interaction between dioxin and carbon nanotubes may be attributed to the unique structure and electronic properties of carbon nanotubes. The carbon nanotubes consist of hexagonal arrays of carbon atoms in graphene sheets that surround the tube axis. Strong interactions between the two benzene rings of dioxin and the surface of the carbon nanotubes are expected. Additionally, the dioxin molecule interacts with all surfaces on the walls of the nanotube within the small pore (i.e., 2.9 nm), and these interaction potentials overlap, resulting in enhanced potentials in the pore. In addition, the strong oxidation resistance of carbon nanotubes is also beneficial for regeneration of the sorbent at high temperatures.

Acknowledgment. We thank Mr. T. Takahashi of NGK Insulators (Japan) for discussions. U.S. Patent pending.

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Use of Carbon Nanofibers in the Removal of Organic Solvents from Water

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Received December 8, 1999. In Final Form: August 3, 2000

Catalytically grown carbon nanofibers are a set of novel structures that are produced by the decomposition of selected carbon-containing gases over metal particles. These conformations consist of nanosized graphite platelets separated a distance of at least 0.34 nm and stacked in various orientations with respect to the fiber axis. Such an arrangement results in a unique structure that is composed of an infinite number of extremely short and narrow pores, suitable for the sequestering of small molecules. We have attempted to capitalize on this blend of properties by using such structures for the selective removal of organic contaminants from aqueous streams. Experimental results indicate that nanofibers possessing a structure in which the graphite platelets are aligned perpendicular to the fiber axis and possessing a high degree of structural perfection exhibit superior selective adsorption properties with respect to removal of alcohols from aqueous media over those displayed by active carbon. Adsorption was enhanced when the carbon nanofibers were initially subjected to a treatment in 1 M hydrochloric acid. In contrast, when this step was carried out in the presence of 1 M nitric acid, the beneficial properties of the nanofibers were effectively suppressed. An analogous series of experiments carried out with nanofibers possessing a structure in which the graphene layers were oriented at an angle with respect to the fiber axis did not result in the same degree of selective capture of the alcohols. A rationale is presented to account for this diverse pattern of behavior.

Introduction

The manufacturers of specialty chemicals and pharmaceuticals generate effluent streams that contain trace amounts of aromatic and chlorinated hydrocarbons. Careful handling, recovery, or disposal of these toxic organics is one of the major environmental issues that confront such industries. Methods for the elimination of such contaminants from gaseous and liquid effluent streams are normally based on fixed-bed adsorption on carbonaceous materials. Traditionally, when recovery steps prove to be uneconomical or difficult, destruction of the organic contaminants is carried out by incineration. Such procedures, however, require elevated temperatures with associated high fuel costs. Catalytic degradation of organic contaminants into less toxic products may be an alternative low-temperature option. An effective catalyst is one on which the contaminant is initially strongly adsorbed and on which reaction with atomic species generated by the interaction of metallic components with the aqueous environment takes place.¹

Activated carbons are the most universal sorbents for purifying water. Their high capacity for adsorption is directly related to their highly porous structures and the presence of surface chemical groups. Both these properties can be modified by either heating or chemical treatments.^{2–4} The nature of the oxygen-containing groups on carbon surfaces has been the subject of considerable

study. The most common groups are carboxyl, lactonic carbonyl, and phenolic functionalities.^{5–7} These groups are acidic, and their density and strength can be determined by selective neutralization techniques.^{3,5,8} They are formed during treatment of the carbon in the oxidant at between 300 and 500 °C and undergo thermal decomposition to CO₂ at higher temperatures. If the oxidation process is performed at temperatures above 750 °C, then basic groups (pyrone-like structures) are produced,⁹ which eventually decompose to form CO. Carbonaceous solids in their pristine state and free of surface oxygen species are hydrophobic in nature. Following oxidative activation, these materials develop some hydrophilic character. Recent studies by Japanese workers^{10–12} have demonstrated that, following plasma treatment in either oxidizing or nonoxidizing environments, the surfaces of carbon structures became extremely hydrophilic and exhibited strong wetting characteristics with respect to water. They reported that an oxygen plasma introduced acidic groups onto the carbon surface, while nitrogen and ammonia plasmas produced basic functionalities.

Activated carbon is used to purify air contaminated with organic vapors. The adsorption capacities of activated carbons for over 120 organic vapors in dry air have been compiled.¹³ Also of interest is the removal of organic contaminants from water. Oda and Yokokawa^{14,15} dem-

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onstrated that the ability of activated carbon to adsorb a variety of organic compounds from aqueous solutions was linked to the surface acidity of the adsorbent. This point was also highlighted by Esumi and co-workers,^{11,16} who modified the surface functionality of carbon by treatment in various plasmas. Recently, there has been a growing interest in other forms of carbon, particularly so-called fibrous activated carbon (FAC), as potential adsorbents for the removal of both aqueous and gas-phase contaminants.¹⁷⁻¹⁹ The performance of FAC based on adsorption capacities and velocities of fluids passing through the solvent is generally superior to that of granular activated carbon.¹⁸⁻²⁰ FAC also appears to be much more selective for low-molecular-weight compounds,²¹ and it was claimed that this aspect was associated with the molecular size of the organic adsorbate.²²

While activated carbons are effective for the adsorption of gaseous molecules, these materials can indiscriminately adsorb not only the contaminant but also water molecules, and consequently, the available volume for the undesirable organic molecules is greatly reduced. This form of carbon is produced by carbonization of polymeric organic precursors, and under such conditions, the structure obtained is primarily amorphous in nature. Graphite—a highly ordered form of carbon—is a solid that possesses delocalized π electrons on the basal planes, and this property imparts a weak basic character to the material in which the polarity can be manipulated by selected chemical treatments. It is these features that, when combined with its hydrophobic nature, enable graphite to adsorb organic molecules in preference to water. Unfortunately, in its conventional form of flat sheets, graphite has a relatively low surface area-to-mass ratio ($\sim 0.5 \text{ m}^2/\text{g}$), which has limited its use as a selective adsorption agent.

We have attempted to overcome the shortcomings of active carbon and graphite by using carbon nanofibers (CNFs), a new type of fibrous carbon material, that has been developed in our laboratory from the metal-catalyzed decomposition of certain hydrocarbons.²³⁻²⁸ In this investigation we have explored the potential of CNFs for the selective removal of organic molecules from aqueous solutions. Graphite nanofibers vary from 5 to 100 μm in length and are between 5 and 100 nm^2 in cross-sectional area.²⁹ High-resolution transmission electron microscopy studies have revealed that the nanofibers consist of extremely well ordered graphite platelets,³⁰ which are oriented in various directions with respect to the fiber axis. The arrangement of the graphene layers can be

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tailored to a desired geometry by choice of catalyst system and reaction conditions. One can therefore generate structures in which the layers are oriented in a "ribbon", "herringbone", or "stacked" arrangement. One of the most outstanding features of these structures is the presence of large numbers of edges, which constitute sites for chemical or physical interaction, particularly adsorption.

An unexpected finding is that such highly ordered crystalline solids exhibit relatively high surface area-to-mass ratios ($100-250 \text{ m}^2/\text{g}$) that can be enhanced by careful activation up to $700 \text{ m}^2/\text{g}$.³¹ By careful choice of the catalyst and reaction conditions, it is also possible to generate structures in which the spacing between graphite platelets can be expanded. In the pristine condition, the distance between graphite layers is 0.34 nm. This spacing can be increased by introducing selected groups between the layers, a process known as intercalation, thereby generating new types of sophisticated molecular sieves.

Experimental Methods

Preparation of Graphite Nanofibers. CNFs were synthesized from the interaction of ethylene/hydrogen (4:1) mixtures over Cu-Ni (3:7) powdered catalysts and carbon monoxide/hydrogen (4:1) mixtures over Fe powdered catalysts. In a typical experiment, 50 mg of the metal powder was placed in a ceramic boat, positioned in the center of a quartz reactor tube heated by a Lindberg horizontal furnace. Prior to reaction with the hydrocarbon mixture, the metal particles were reduced in a 10% H₂/He mixture at 600 °C for approximately 2 h. Hydrogen was eliminated from the tube by flushing with helium, and then the carbon-containing gas/hydrogen mixture (4:1) was introduced at a total flow rate of 200 sccm and the reaction vessel was maintained at 600 °C. The reaction was allowed to continue for 1 h, the reactant gas mixture was stopped and replaced with helium, and the system was allowed to cool to room temperature. Surface area measurements were conducted in a 100CX Coulter adsorption unit. Samples were initially outgassed at 10^{-7} Torr at ambient temperature for about 4 h. Following this step, samples were heated to 160 °C and maintained under vacuum for approximately 8 h. Once the solids were cool, nitrogen adsorption measurements were performed at -196 °C. All of the samples were subjected to an identical set of treatments.

Initial adsorption experiments were conducted on pristine nanofibers, and their abilities to take up selected organics from aqueous solutions were compared to those of active carbon under the same conditions. In further studies the effects of pretreatment in various acid media on the subsequent adsorption characteristics of the nanofibers were investigated. For these experiments the CNF samples were allowed to soak in 1 M aqueous solutions of either hydrochloric or nitric or 0.5 N sulfuric acids for periods of up to 3 weeks. The nanofibers were then thoroughly washed in deionized water before being dried overnight at 110 °C and then stored in sealed vessels.

The CNF samples were characterized using a variety of methods including high-resolution transmission electron microscopy, X-ray diffraction, and temperature-programmed oxidation techniques. The details of the structural characteristics of the material were obtained from high-resolution TEM examinations performed in a JEOL 2000 EXII instrument capable of 0.18 nm lattice resolution. Suitable transmission specimens were prepared by application of a drop of ultrasonically dispersed nanofibers in isobutanol onto a holey carbon support film.

Powder X-ray diffraction patterns of the acid-treated CNF samples were obtained with a Scintag diffractometer using nickel-filtered Cu K α radiation at a scan rate of 1.5°/min, and peaks were identified by comparison with standards in a related computer database. Diffraction patterns were recorded over a range of 2 θ angles from 10 to 90° and compared with the known spacings of graphite. Finally, the BET surface areas of the

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nanofibers, calculated from N_2 adsorption at -196°C , were measured using a Coulter Omnisorb 100 CX unit.

Adsorption Studies. Adsorption of selected organic compounds from aqueous solutions was evaluated according to the following protocol. In a typical experiment, 0.2 g of the carbonaceous solid was placed in a solution containing 0.5 mL of alcohol in 60 mL of deionized water. The mixture was continuously stirred and maintained at room temperature for periods of up to 160 h. The reaction vessel was sealed throughout the process to prevent loss of the alcohol due to evaporation. The uptake of alcohol by the carbonaceous solid was monitored as a function of time by taking samples of the solution at various intervals of time, which were subsequently analyzed by gas chromatography. Identical experiments were conducted using an active carbon sample possessing a surface area of about 7.5 times that measured for the CNF samples. In addition, blank experiments were performed with alcohol/water mixtures in the absence of any carbon material.

Results and Discussion

Characterization of the Carbon Nanofibers. *Transmission Electron Microscopy Studies.* Examination by TEM of the carbonaceous solids produced from the metal-catalyzed decomposition of carbon-containing gases indicated that they consisted exclusively of nanofibers, with no indication of any other forms of carbon being present. These undesirable forms of carbon are frequently found when high-temperature noncatalytic methods were used for the synthesis of the nanostructures. High-resolution TEM studies revealed that the samples generated from the interaction of CO/H_2 with Fe were highly graphitic structures in which the graphene sheets were aligned perpendicular to the fiber axis, as shown in Figure 1a. A schematic representation of the three-dimensional structural conformation of this type of material is shown in Figure 1b. On the other hand, nanofibers that were grown from the interaction of ethylene with Cu–Ni bimetallic catalysts exhibited the so-called “herringbone” configuration shown in the electron micrograph and schematic representation, Figure 2a and b, respectively.

It should be noted that the nanofibers generated from the interaction of $\text{C}_2\text{H}_4/\text{H}_2$ with Cu–Ni catalysts possessed significantly more structural imperfections than those synthesized from the decomposition of CO/H_2 over Fe powders. In both cases, however, the width of the nanofiber corresponded to that of the cross-sectional area of the catalyst particle responsible for its growth. The structural perfection of carbon nanofibers has been related to the strength of the interaction of the metal catalysts with the basal plane of graphite.²² Wetting and spreading of a particle on a support occurs at a temperature that is dependent on various parameters including the nature of the substrate and the composition of the reactant gas. This is the point where the maximum affinity between the metal and the support is achieved. Under the reaction conditions used in the experimental setup, metal particles undergo rearrangement so as to generate faces in which the interstices are perfectly matched with the atomic arrangement of single-crystal graphite and, as a consequence, the deposited carbon will possess a high degree of crystalline perfection. This reconstruction occurs when Fe particles are allowed to interact with CO/H_2 at 600°C .²⁴

X-ray Diffraction Measurements. X-ray patterns of the two types of pristine nanofibers showed that the “platelet” form (shown in Figure 1) was highly graphitic in nature with a d -spacing very close to that of single-crystal graphite (0.335 nm) (see Figure 3). On the other hand, the “herringbone” material (shown in Figure 2) contained more imperfections, as evidenced by the wider d -spacing

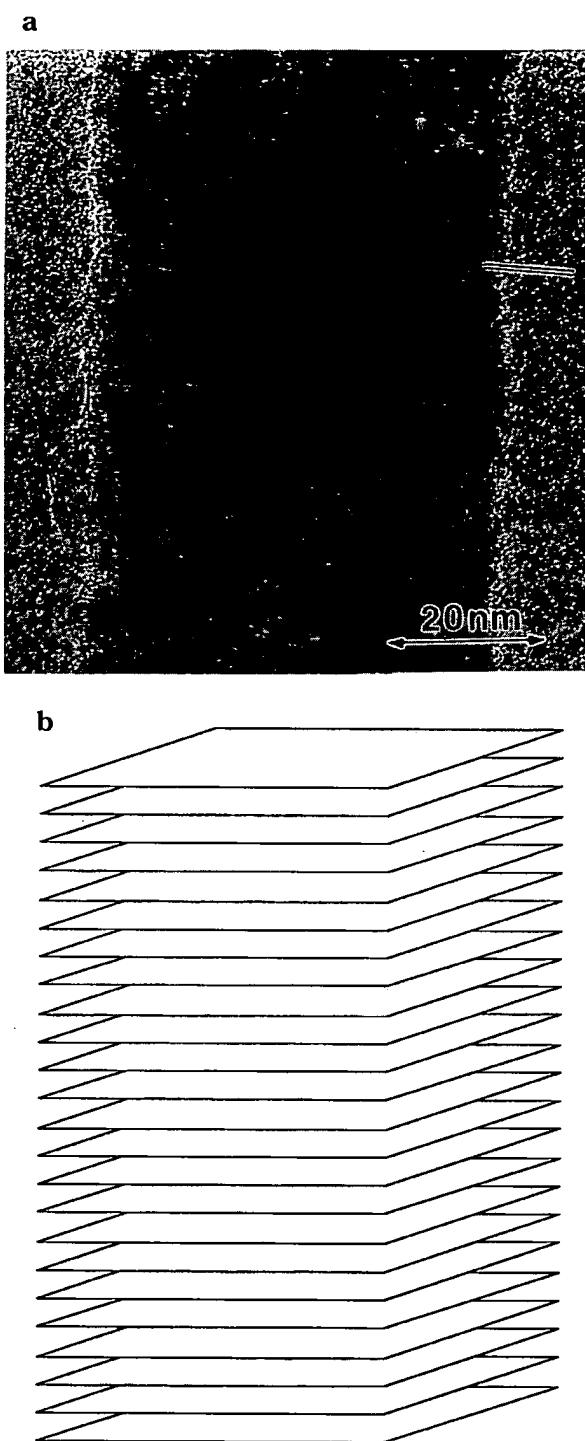


Figure 1. (a) High-resolution transmission electron micrograph of the “platelet” form of CNFs (the direction of the graphene sheets is indicated). (b) Three-dimensional rendition of “platelet” CNFs showing the stacking of graphite platelets in CNFs.

distribution (Figure 4). The average stack height, L_c , was determined from the broadening of the principal graphite peak (the 002 reflection), and these values along with the analogous values obtained from various acid treatments of the two types of materials are presented in Table 1. Inspection of these data reveals that, as expected, the more disordered “herringbone” structures have a relatively short stack height. It is interesting to find that the various

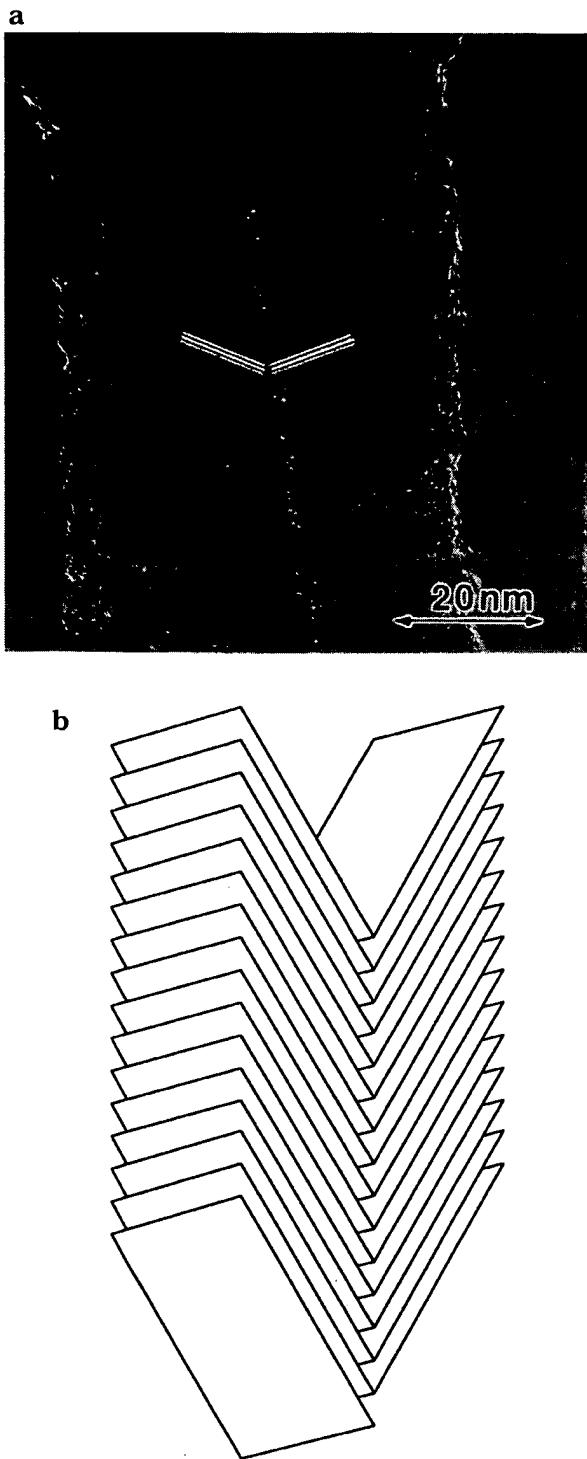


Figure 2. (a) High-resolution transmission electron micrograph of the "herringbone" form of CNFs (the direction of the graphene sheets is indicated). (b) Three-dimensional rendition of "herringbone" CNFs indicating the arrangement of graphene

acid treatments did not affect the d -spacing but did tend to disrupt the structural integrity of the "platelet" nanofibers. On the other hand, a significant expansion in the lattice spacing was observed following adsorption of butanol into this type of material, which suggests that the organic molecule "slides" between two graphene layers, causing the structure to undergo an expansion.

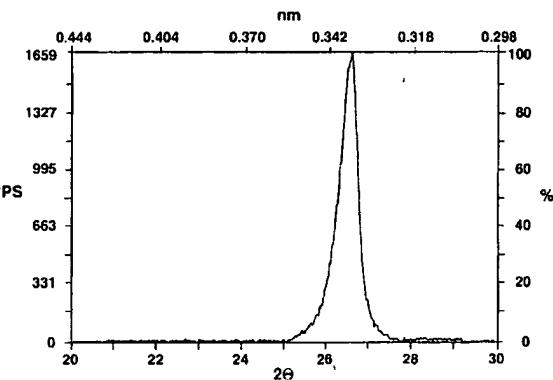


Figure 3. X-ray diffraction pattern of "platelet" CNF structures.

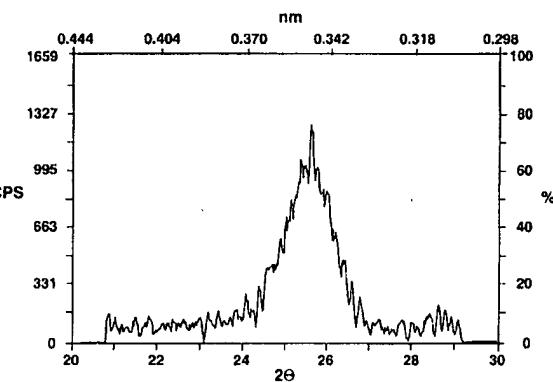


Figure 4. X-ray diffraction pattern of "herringbone" CNF structures.

Table 1. Structural Characteristics of Pristine and Acid-Treated "Platelet" and "Herringbone" CNF Materials Obtained from X-ray Diffraction Studies

type of CNF ^a	treatment	mean d spacing (nm)	stack height, L_c (nm)
P-CNF	pristine	0.335	17.5
P-CNF	HNO_3	0.336	12.8
P-CNF	HCl	0.338	13.8
P-CNF	H_2SO_4	0.340	15.6
P-CNF	HCl/ethanol adsorption	0.338	14.0
P-CNF	HCl/butanol adsorption	0.344	10.8
H-CNF	pristine	0.347	5.4
H-CNF	HNO_3	0.346	4.7
H-CNF	HCl	0.347	4.6
H-CNF	H_2SO_4	0.349	5.6

^a P-CNF, platelet carbon nanofiber; H-CNF, herringbone carbon nanofiber.

Surface Area Determinations. BET measurements using nitrogen at $-196\text{ }^\circ\text{C}$ are presented in Table 2 and indicate that the surface area of the "platelet CNF" was $119.1\text{ m}^2\cdot\text{g}^{-1}$, while that of the "herringbone" form was $161.3\text{ m}^2\cdot\text{g}^{-1}$. In contrast, the active carbon sample exhibited a significantly higher value of $646.3\text{ m}^2\cdot\text{g}^{-1}$. Subsequent treatment of both types of CNF materials in 1 M hydrochloric acid resulted in an increase of the surface area of the H-CNF but had little impact on the value of the P-CNF. On the other hand, when this process was conducted in 1 M nitric acid, a reduction in the surface area of the P-CNF was observed with no change in the value of the H-CNF. Loss of active sites as a result of nitric acid treatment may be due to the formation of oxygenated species that can cross-link at the edge regions of the graphite sheets. Immersion of the nanofibers in 0.5 M sulfuric acid appears to cause an increase in the

Table 2. Surface Areas of Pristine and Acid-Treated "Platelet" and "Herringbone" Types of Carbon Nanofibers

material ^a	BET N ₂ surface area (m ² /g)	micropore ^b surface area (%)
Norit carbon	646.1	81.85
P-CNF (pristine)	119.1	6.9
P-CNF (HCl treated)	112.92	46.4
P-CNF (HNO ₃ treated)	60.48	66.8
P-CNF (H ₂ SO ₄ treated)	82.16	40.0
H-CNF (pristine)	161.3	25.6
H-CNF (HCl treated)	257.3	66.7
H-CNF (HNO ₃ treated)	161.7	77.45
H-CNF (H ₂ SO ₄ treated)	187.7	60.2

^a P-CNF, platelet carbon nanofiber; H-CNF, herringbone carbon nanofiber. ^b Less than 2.0 nm.

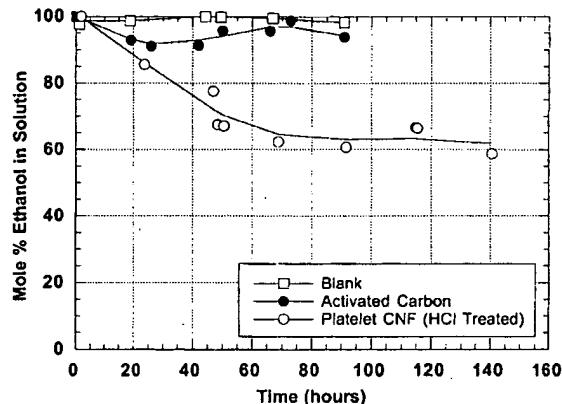


Figure 5. Comparison of the adsorption characteristics of ethanol as a function of time at 25 °C on various types of carbon materials.

interlayer spacing of both materials and, in contrast to the nitric acid treatment, does not have a deleterious effect with respect to loss of active sites. It was interesting to find that no equivalent changes were apparent when the active carbon sample was given the same series of acid treatments. The T-plot analysis of the isotherms developed by Lippens and co-workers³² was used to calculate the micropore volume of all carbon samples. By extrapolating the second linear region of the *y*-axis, it was possible to estimate that over 80% of the total surface area of activated carbon consisted of micropores. On the other hand, the micropore volume of CNFs varied from as little as 7 to as high as 77%. It would appear that the surface chemistry of these structures has an effect on the shape of the isotherm, that ultimately alters the value of the micropore volume, leading to inaccurate results. This extraordinary behavior is not fully understood at present. It should be stressed, however, that since the determination of this parameter was accomplished using nitrogen (kinetic diameter 0.364 nm) as the adsorbate, accessibility to the inner sections of the CNF was not realized and, consequently, ultra-microporosity—within the walls of the nanofibers—was not measured.

Adsorption of Organic Molecules on "Platelet" CNFs. In the first series of experiments, we examined the adsorption of ethanol on active carbon and "platelet" CNFs treated with 1 M HCl. The results presented in Figure 5 show that the ability of the nanofibers to adsorb the alcohol far exceeds that of active carbon. After a period of about 60 h, the uptake of ethanol on active carbon was only 6%, whereas 38% was achieved on the nanofibers.

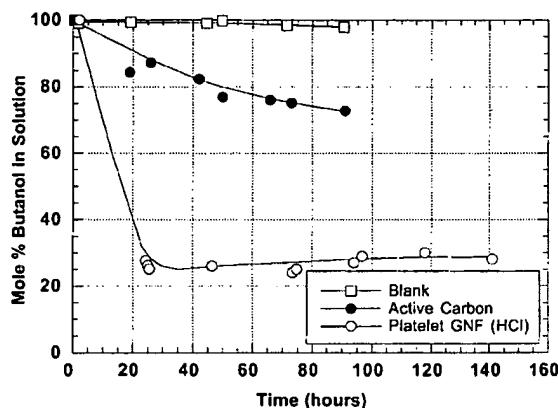


Figure 6. Comparison of the adsorption characteristics of butanol as a function of time at 25 °C on various types of carbon materials.

Although active carbon has a much larger surface area, it is apparent that adsorption of the organic from an aqueous solution is nonselective in nature: an indication of the low affinity of these solids toward the alcohols molecules. On the other hand, due to the chemical character of CNF, which consists entirely of graphite platelets, we believe that it is possible for relatively narrow molecules to "slide" between the layers where they interact with the basal plane regions of the material. Indeed, although ethanol has some polarity, the molecule is known to be capable of wetting graphite due to such interactions. Water molecules should have negligible affinity for the basal plane of graphite and so do not have access to the inner structure.

In a second series of experiments, the removal of butanol from an aqueous solution was investigated on both types of carbon materials, and these data are presented in Figure 6. Again the acid-treated CNF exhibited a superior adsorption of the alcohol compared to that of active carbon. In this experiment the nanofibers removed 75% of the butanol from solution in about 25 h. In contrast, active carbon adsorbed only about 28% of the butanol over 90 h. These results emphasize the importance of structure on the selective adsorption of organic molecules from water. Although the active carbon used in the present investigation possesses a surface area that is over six times larger than that of the nanofibers, its capacity for adsorption of nonpolar molecules is quite inferior to that of the CNF. One may therefore infer that the CNF consists of two main regions that result in an array of hydrophobic nanopores with slightly polar edges resembling a micellar structure that has a high affinity for nonpolar substances while suspended in and in intimate contact with aqueous media. The existence of this unique conformation is evidently quite effective for selective adsorption processes.

Adsorption of Organic Molecules on Acid-Treated "Platelet" CNFs. Our investigation of the influence of acid pretreatment on the adsorption characteristics of the nanofibers included studies of samples immersed for 60 h in hydrochloric or nitric acid. The sorption data for ethanol and butanol (Figure 7) reveal that these treatments induce dramatic differences in the adsorption characteristics of the nanofibers toward the two alcohols. Immersion in 1 M hydrochloric acid appears to activate the nanofibers toward adsorption of both ethanol and butanol from an aqueous solution. A somewhat unexpected finding was that when the "platelet" CNF samples were treated in nitric acid, their ability to selectively adsorb particular alcohols was seriously impaired. The latter

(32) Lippens, B. C.; Linsen, B. G.; de Boer, J. H. *J. Catal.* 1964, 3, 32.

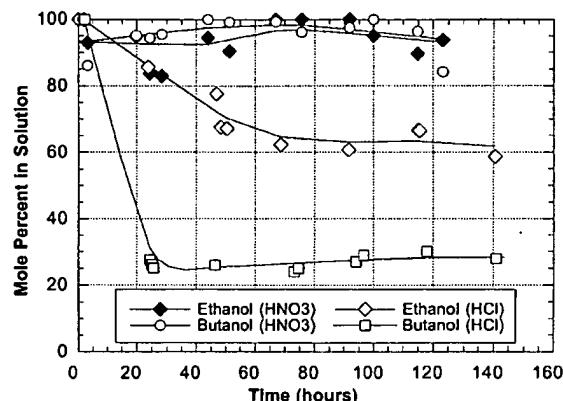


Figure 7. Comparison of the adsorption characteristics of ethanol and butanol as a function of time at 25 °C on platelet CNFs that have been treated in various acids.

Table 3. Adsorption of Organic Compounds from Aqueous Solution on Various Carbon Materials after 60 min of Interaction

material	% adsorbed		
	ethanol	butanol	pentanol
active carbon	21.0	22.9	10.9
H-CNF (pristine)	14.3	15.5	9.0
H-CNF (HCl treated)	0.5	14.8	6.0
H-CNF (HNO ₃ treated)	0.9	8.5	7.4
H-CNF(H ₂ SO ₄ treated)	0.0	17.0	6.0
P-CNF (HCl treated)	32.0	75.0	
P-CNF (HNO ₃ treated)	2.0	0.0	

treatment may have introduced oxygenated groups at the edge regions of the platelets, making them more hydrophilic. Water molecules may adsorb and seal off the edges, preventing the penetration by alcohol molecules to the hydrophobic interior. Cross-linking reactions between the polar groups may further inhibit penetration of the inner parts of the fibers.

The ability of CNF to adsorb organic molecules is in agreement with previous work performed by Fenelonov and co-workers,³³ who investigated the selective adsorptive properties of catalytically grown filamentous carbon (CGFC) using gas chromatography. They reported that CGFC exhibited a capacity up to 10¹⁰ times higher than that of graphitized carbon black for the uptake of benzene and up to 10¹² times higher for heptane.

Adsorption of Organic Molecules on "Herringbone" CNFs. When "herringbone" nanofibers possessing a structure with a short range crystallographic order were utilized as the adsorbate medium, an extremely poor performance for the selective removal of the organic constituents from the aqueous solution was observed. The adsorption capacity of these materials was below that observed for activated carbon, as shown in Table 3. In addition, these values were substantially smaller than those attained when "platelet" CNFs were used as the adsorbate.

When "herringbone" CNFs were subjected to acid treatments, their performance toward the adsorption of ethanol was practically suppressed and the adsorption of pentanol was significantly reduced. Although the capacity of "herringbone" CNFs toward the removal of butanol from solution was smaller than that observed with active carbon, some interesting trends can be seen in these

(33) Fenelonov, V. B.; Avdeeva, L. B.; Goncharova, L. G.; Okkel, P. A.; Simonov, A. D.; Derevyankin, A. Yu; Likholobov, V. A. *Preparation of Catalysts VI*; Poncelet, G., Eds.; 1995; p 825.

Table 4. Weight Change of CNF Following Exposure to Liquid Water at 25 °C until Saturation

material	wt % change
H-CNF	1075
P-CNF	486
Norit carbon	130

systems. Whereas treatment of "herringbone" CNFs in nitric acid completely suppressed the butanol adsorption, hydrochloric acid had no impact, and H₂SO₄ appeared to slightly improve the uptake with respect to the pristine material. Sulfuric acid is known to intercalate graphite^{34–37} in a process that involves the ingress of groups within the layers, which results in a change of the *d*₀₀₀₂ interplanar distance to produce a more "open" conformation. This is indeed confirmed by X-ray diffraction measurements that are presented in Table 1. It can be seen that treatment in H₂SO₄ resulted in a slight increase in the *d*-spacing from 0.335 to 0.340 nm for "platelet" and from 0.347 to 0.349 nm for "herringbone" CNFs. In a final investigation, the active carbon sample was subjected to the same three acid treatments and its subsequent adsorption behavior compared to that of the unadulterated material. In this case, none of the acid treatments appeared to alter the adsorption of the alcohol from aqueous solutions.

The relationship between the structure of the adsorbate and its "adsorbability" onto fibrous activated carbon was proposed by Brasquet and co-workers.³⁸ These workers, however, refer to a physical conformation more than a true structural feature of the adsorbent materials. The effect of the structure of the carbon, however, has not been previously investigated, since the existence of highly crystalline nanofibers and a large scale synthesis process has only recently been disclosed.^{29,39} Another aspect of importance when dealing with adsorption properties of solids is the effect of surface functionality that can favor the interaction of the material with water. Indeed, it was found that when the various carbon solids used in the present investigation were saturated with water, the ability to retain the solvent was dependent upon the nature of the solid, and this aspect is illustrated in Table 4. Evidently, herringbone CNFs exhibited the highest retention capacity of the three solids with a surprisingly low value observed for the high-surface-area activated carbon. We believe that, due to the saturation of the surface with water, access of the organic solvent to the inner portions of the nanofibers is effectively blocked. This would explain why the herringbone nanofibers exhibited such a poor performance toward the adsorption of organic molecules. Table 5 shows a comparison of the behavior of the various carbons toward selective adsorption of alcohols from aqueous solutions. The surface coverage factor—defined as the percent of organic component adsorbed with respect to the surface area of carbon—is a normalized value intended to correlate the effectiveness of a given solid toward adsorption of a given compound. In this regard, it is evident from the data presented in Table 5 that the performance of P-CNF is superior to that of the other carbon materials used in this investigation, despite the fact that the former has a much lower surface area.

(34) Moissette, A.; Fuzellier, H.; Burneau, A. *Mater. Sci. Forum* 1992, 91/93, 95.

(35) Guoqiang, L.; Daozhi, L.; Huafu. *Carbon* 1992, 30, 961.

(36) Monyakina, L. A.; Avdeev, V. V.; Nikol'skaya, I. V. *Inorg. Mater.* 1990, 26, 637.

(37) Brandt, N. B.; Kul'bachinskii, V. A.; Lapin, S. A. *Sov. Phys. Solid State* 1990, 32, 51.

(38) Brasquet, C.; Subrenat, E.; LeCloirec, P. *Water Sci. Technol.* 1997, 35, 251.

(39) Murayama, H.; Maeda, T. *Nature* 1990, 345, 791.

Table 5. Relative Surface Coverage of the Adsorbates on Various Carbons

adsorbate	log K_{ow}^a	surface coverage factor over various carbons ^b		
		P-CNF	H-CNF	Norit carbon
ethanol	-0.32	0.38	0.11	0.032
butanol	0.88	0.63	0.10	0.036
pentanol	1.4		0.06	0.016

^a Octanol/water partition coefficient. ^b Surface coverage factor = % adsorbed organic/surface area of carbon. ^c Data taken following adsorption for a period of 60 min.

Furthermore, taking into account the octanol–water partition coefficient of the three alcohols, it becomes apparent that the degree of hydrophobicity increases as the molecular weight of the organic increases, and this aspect is reflected in the better performance of the P-CNF material for this process. These results highlight the importance of the structure of the adsorbent on the adsorption process and more importantly in its selectivity, a feature that had not been previously demonstrated because of the difficulty of obtaining carbon materials possessing a truly uniform architecture.

The present study demonstrates that while the molecular structure of the adsorbate is an important feature, the degree of crystalline perfection of the solid carbon adsorbent must also be taken into consideration when designing a material for selective adsorption. A combination of these two factors would therefore provide the best adsorption performance in novel filtration devices.

Summary

Carbon nanofibers possessing a high degree of crystalline order in which graphene sheets are stacked in a direction perpendicular to the fiber axis have been found to exhibit excellent adsorption characteristics for the removal of small amounts of alcohols from aqueous

solution. Experiments show that even though the so-called "platelet" nanofibers have a surface area that is almost an order of magnitude lower than that of active carbon, their performance for this separation process is far superior to that displayed by the latter material. A further feature to emerge from this work is the finding that pretreatment conditions exert a crucial effect on the subsequent adsorption behavior; while prolonged immersion in hydrochloric acid was found to be extremely beneficial, a similar treatment in nitric acid virtually nullified the advantages of using nanofibers for the process.

When a corresponding set of experiments were carried out with carbon nanofibers that possessed a more disordered structure and where the alignment of the graphene sheets was at an angle to the fiber axis, only a mediocre performance was achieved. Indeed, for the most part, the adsorption characteristics of this type of nanofibers were comparable or inferior to those exhibited by active carbon under the same conditions. It is postulated that during immersion in aqueous media the "herringbone" CNF structures tend to lose their hydrophobic nature and, as a consequence, do not exhibit selective adsorption properties with respect to organic contaminants.

The results of the present investigation have indicated that CNFs constitute a unique adsorption system, where nonpolar molecules can be effectively removed from aqueous solutions to be trapped inside slit-shaped pores. X-ray diffraction measurements of CNF indicated that, following adsorption of organic molecules, widening of the pores occurred, as established by the measured increase of the d_{0002} interplanar spacing.

Acknowledgment. Funding for this work was provided by the U.S. Department of Energy, through Grant DE-FG07-96ER14688.

LA9916068